Investigation of factors affecting gaseous mercury concentrations in soils

Christopher W. Moore [a], Mark S. Castro [b],*

[a] Division of Atmospheric Science, Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, United States
[b] Appalachian Laboratory, University of Maryland Center for Environmental Science, 301 Braddock Road, Frostburg, MD 21532, United States

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ABSTRACT

The purpose of this study was to determine the effects of soil temperature, soil moisture, redox potential (Eh) and soil organic matter (SOM) on the total gaseous mercury (TGM) concentrations in background soils. Our measurements were made in a grass field and deciduous forest at the Piney Reservoir Ambient Air Monitoring Station (PRAAMS) in Garrett County, Maryland. Three plots in each area were sampled every third week from July 2009 to June 2010 at the Oe–A soil horizon interface, the A–E soil horizon interface, and 5 and 10 cm into the E soil horizon. The mean soil TGM concentration for all depths in the forest (2.3 ± 2.2 ng m^{-3}) was significantly higher than the mean soil TGM concentration in the grass field (1.5 ± 1.9 ng m^{-3}). Soil TGM at all depths was most strongly and consistently correlated to soil temperature. The soil TGM concentrations were highest and most variable at the forest Oe–A soil horizon interface (4.1 ± 2.0 ng m^{-3}), ranging from 1.5 to 8.4 ng m^{-3}. This soil horizon interface had 11 to 26% more SOM and the soil Eh was 100 to 400 mV lower than the other soil depths. Our results suggest that soil temperature, soil Eh and SOM are significant factors affecting TGM concentrations in forest soils. Future studies of TGM dynamics in background soils may benefit from closely monitoring the organic soil horizon.

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1. Introduction

The size and dynamics of the gaseous mercury pool in soils may play an important role in the atmospheric fluxes of mercury (Johnson and Lindberg, 1995; Moore et al., 2011; Sigler and Lee, 2006; Zhang and Lindberg, 1999). Many processes in soils may influence the conversion between Hg(II) and gaseous elemental mercury (GEM), which can be released into the atmosphere (Zhang and Lindberg, 1999). Studying the soil gas mercury pool is different than studying atmospheric fluxes of TGM. For example, soil gas mercury concentrations may change much more slowly and be affected by different environmental parameters than soil TGM fluxes. Unfortunately, however, few studies have examined the factors affecting the gaseous mercury pool in background soils (Johnson et al., 2003; Kromer et al., 1981; Sigler and Lee, 2006; Wallschläger et al., 2002).

GEM is semi-volatile at ambient temperatures and the volatility can be an exponential function of temperature (Sigler and Lee, 2006). Many studies have shown that higher soil temperatures can increase the atmospheric fluxes of TGM (Bahlmann and Ebinghaus, 2003; Carpi and Lindberg, 1998; Choi and Holsen, 2009a; Choi and Holsen, 2009b; Edwards et al., 2001; Ericksen et al., 2006; Gillis and Miller, 2000; Gustin et al., 2004; Gustin et al., 1997; Lin et al., 2010; Obrist et al., 2005; Scholtz et al., 2003; Sigler and Lee, 2006; Tsiros, 2002). However, Sigler and Lee (2006) also showed that higher soil temperatures led to higher TGM concentrations in background soils. These higher soil temperatures may have stimulated microbial activity responsible for the reduction of Hg(II) to GEM (Baldi, 1997; Fritsche et al., 2008; Kritee et al., 2008).

Soil organic matter (SOM) has been shown to provide binding sites for Hg(II) (Meili, 1991; Skyllberg et al., 2006). In forest soils, higher amounts of matrix bound mercury are often associated with higher SOM content (Akerblom et al., 2008; Andersson, 1979; Demers et al., 2007; Gabriel and Williamson, 2004; Grigal, 2003; Johansson et al., 1991; Meili, 1991; Obrist et al., 2009; Obrist et al., 2011; Sigler and Lee, 2006; Yin et al., 1997). The Hg(II) bound to SOM may increase soil TGM concentrations, if reduced to GEM (Gu et al., 2011). Sigler and Lee (2006) speculated that SOM may strongly influence TGM concentrations in soils, but they did not measure SOM in their study.

Soil redox potential (Eh) may affect TGM concentrations in soils by influencing the availability of electrons for oxidation–reduction reactions involving Hg(II) and GEM (Andersson, 1979; Gabriel and Williamson, 2004; Obrist et al., 2009; Schluter, 2000; Schuster, 1991; Zhang and Lindberg, 1999). It was speculated that under low soil Eh conditions, the Hg(II) contained in SOM could be reduced to GEM (Andersson, 1979; Gabriel and Williamson, 2004). This reduction may lead to higher TGM concentrations in soils. At higher Eh, GEM can be oxidized to Hg(II), bound to SOM or lost in soil water export (Andersson, 1979; Gabriel and Williamson, 2004; Schuster, 1991). However, little or no information exists on the effects of soil Eh on the formation of GEM in background soils (Schluter, 2000).

* Corresponding author. Tel.: +1 301 689 7163.
E-mail address: mcastro@umces.edu (M.S. Castro).

Increases in soil moisture can affect the movement and formation of TGM in soils (Gustin et al., 2004; Gustin and Stamenkovic, 2005; Lin et al., 2010; Lindberg et al., 1999; Song and Van Heyst, 2005). This effect may be transient, since TGM fluxes have been shown to quickly increase and then decrease in response to precipitation events (Gustin and Stamenkovic, 2005; Lindberg et al., 1999; Song and Van Heyst, 2005). Increases in soil water will often decrease soil Eh, which can increase the reduction of Hg(II) to GEM (Ponnamperum, 1972; Zarate-Valdez et al., 2006). Alternatively, Gustin and Stamenkovic (2005) speculated that more polar water molecule out competes the Hg(II) for binding sites in soils and the Hg(II) is subsequently released from soils into soil water.

Despite the potential importance of the soil TGM pool in the overall cycling of mercury, no studies have simultaneously measured the effects of soil Eh and soil moisture on the TGM concentrations in soils. Also, little information exists on the spatial and temporal variations of the soil TGM pool. Therefore, the purpose of this study was to identify factors that influenced the spatial and temporal patterns of TGM concentrations in background soils.

2. Methods

2.1. Study site

This study was conducted at the Piney Reservoir Ambient Air Monitoring Station (PRAAMS) in Garrett county Maryland (elevation: 781 m) (39° 42′ 21.29″ N, 79° 0′ 43.21″ W). In 2004, the deciduous forest at PRAAMS was selectively harvested in order to establish a large open area for an atmospheric monitoring station. There is currently a suite of atmospheric trace gasses, aerosols, and meteorological parameters measured at PRAAMS. A variety of native grasses, thorns, and flowers now cover the open area, which is mowed when needed. For this study, we established three 3 m by 2 m plots in the open grass field and in the adjacent deciduous forest.

Soils at PRAAMS were Dekalb and Gilpin very stony loams (USDA, 2009). The O horizon was considerably different between the two areas. The forest O horizon extended to a depth of 7 cm and contained more undecomposed organic surface litter (Oi) than the grass field. In the grass field, the O horizon was only 4 cm thick, the Oi layer was very thin (2 mm), and the surface litter consisted of grasses. The A horizons in the two areas were very organic-rich and 6 to 10 cm thick. The E horizons in the two areas started at about 10 cm below the surface. Averaged over all depths, soil pH was significantly lower in the forest (3.99 ± 0.14) than the grass area (4.43 ± 0.17). Soil pH determined with EPA SW-846 Method 9045. In the forest area, the top 25 cm of soil had a mean bulk density of 0.83 g cm^3 (USDA-NRCS, 2011). The mean bulk density for the top 25 cm of soil in the grass area was 1.01 g cm^{-3} (USDA-NRCS, 2011).

2.2. Soil TGM concentrations

Soil TGM concentrations were measured every third week from July 2009 through June 2010 using a new approach described in Moore et al. (2011). Samples were collected twice each day during daylight hours. The measurements represent only the daytime periods and the diurnal variations were not examined. We collected soil gas samples from inverted Pyrex glass funnels installed at the Oe–A soil horizon interface (3–7 cm depth), the A–E soil horizon interface (9–15 cm depth), 5 cm into the E soil horizon (13–20 cm depth), and 10 cm into the E soil horizon (18–25 cm depth) in each plot.

Each sampling period consisted of two consecutive sampling days. On the first day, we randomly sampled one of our sampling areas (grass or forest). The other area was sampled on the second day. These consecutive days were selected to minimize between day differences in precipitation and temperature. On each sampling day, we sampled for 1.5 to 3 h per plot. The 1.5-hour sampling period was only used when we expected significant rainfall because intense rainfall events would flood the shallower funnels. This water would
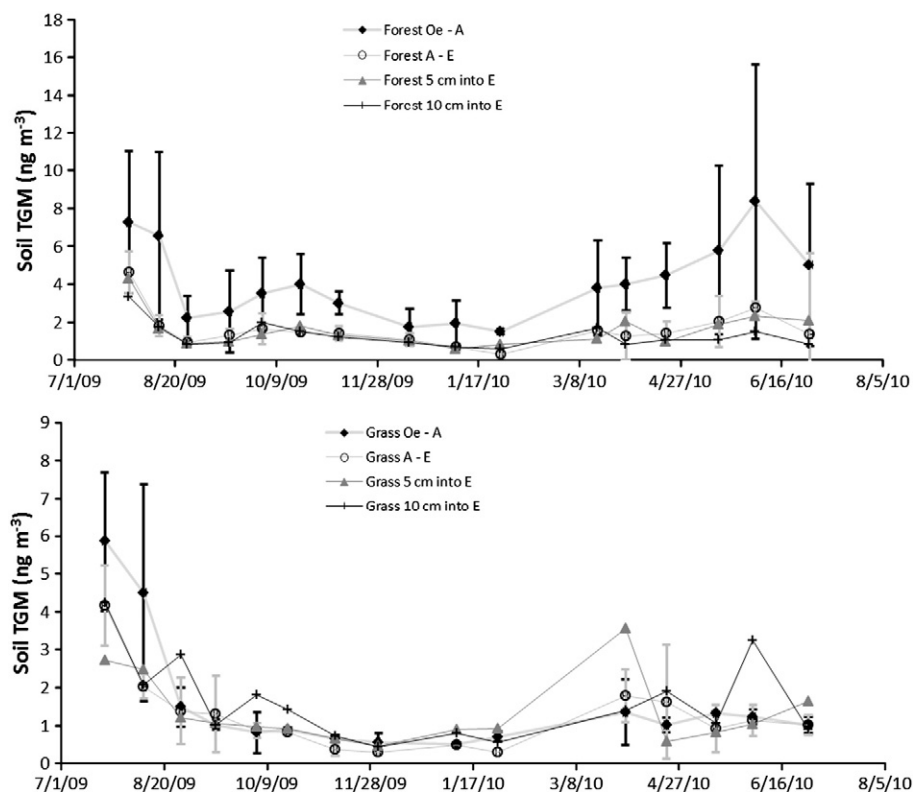

Fig. 1. Mean daily soil gas TGM at all depths in the forest (top) and grass (bottom) areas. Error bars are ± one standard deviation and to simplify the graph error bars are only shown for the Oe–A and A–E soil interface layers (layers with highest standard deviation).

then be sucked into our sampling system, which would destroy our mass flow controller. During the second sampling of each day, one of the two plots sampled earlier in the day was re-sampled. This pattern allowed one plot to be sampled twice on each sampling day. We also randomly selected the order in which the plots would be sampled to prevent a sampling bias. However, in the forest area on 1/6/2010 and 1/28/2010, there was only one sampling period due to heavy snow and limited daylight. This meant that one of the three plots was not sampled and there was no replicate. On 1/9/2010 and 1/29/2010 in the grass area, not all funnels were sampled because of ice in these funnels. Note that for all sampling dates, soil gas TGM concentrations were not significantly different between the first and second sampling periods.

Mercury in soil gas was collected on gold coated quartz sand traps by pumping air out of each funnel at 25 mL min^{-1} (Moore et al., 2011). This flow rate was used to eliminate entrainment of ambient air and to avoid creating an artificial TGM concentration gradient (Fang and Moncrieff, 1998; Sigler and Lee, 2006). Flows for each funnel were controlled with a separate rotameter that was calibrated using a BIOS Definer 220 at the beginning of each sampling period and when switching between plots. Nine rotameters were used to sample eight funnels and ambient air simultaneously. This also allowed us to sample all depths in two plots simultaneously.

We determined the mass of the total mercury collected on the gold traps (m_{Hg}) by thermal desorption into a Tekran 2500 mercury detector. The mass of mercury desorbed from the gold traps was between 2.5 and 20 pg. This was a factor of 2.5 and 200 above the detection limit of the Tekran 2500 (0.1 pg). All analyses, except on 7/22/2009 in the grass area and 7/28/2009 in the forest, were performed on the day of sample collection. The detector was calibrated with a Tekran 2505 mercury vapor calibration unit and a digital syringe (1702RN, 25 μL, Hamilton Co.) (Moore et al., 2011). The soil TGM concentrations were determined with the equation: TGM (ng m^{-3}) = m_{Hg} (ng)/flow rate (m^3 min^{-1})/time sampled (min).

2.3. Soil Eh

Soil Eh probes were constructed from 10 gage copper and 0.5 mm platinum wires (Rabenhorst et al., 2009; van Bochove et al., 2002; Wafer et al., 2004). Initially, five Eh probes were deployed at the A–E soil horizon interface, 5 cm into the E soil horizon and 10 cm into the E soil horizon in all plots in both areas. All Eh probes were deployed within 1.5 m of our soil TGM measurement funnels. The signal from these Eh probes was compared to a Ag/AgCl half-cell reference electrode (Rabenhorst et al., 2009). The probes were monitored every 10 min with a Campbell Scientific CR10X. After the 10/21/2009 sampling, we realized that the highest and most variable soil TGM concentrations were in the Oe–A soil horizon interface. On 11/9/2009, we deployed 10 soil Eh probes at this interface. These 10 probes were deployed on the day of sampling, then removed and redeployed on the next sampling date. The Oe–A horizon probes were monitored with a separate CR10X and Ag/AgCl reference electrode. They were also deployed within 1.5 m of the soil TGM funnels. Soil Eh was not measured at the lower three depths in the forest area on 11/9/2009 due to equipment problems. On 1/6/2010 in the forest and 1/9/2010 and 1/29/2010 in the grass area, soil Eh was not measured in order to keep the reference electrode from freezing.

2.4. Soil temperature, moisture, bound total mercury, and organic matter

Soil temperature and soil moisture was measured with 5 cm long Decagon Devices 5TE probes (Decagon Devices, Inc., Pullman, WA, USA). One sensor was installed at the Oe–A soil horizon interface, A–E soil horizon interface, and 5 and 10 cm into the E horizon in each plot for both areas. We calibrated these soil moisture probes in our laboratory using the protocols provide by Decagon Devices, Inc.

To determine soil bound total mercury concentrations and SOM content, 0.5 kg soil samples were collected from each depth in each plot on 7/8/2010. SOM content was determined by loss on ignition (LOI) (Nelson and Sommers, 1996). For soil bound total mercury determination, 1 g sub-samples were placed into 40 mL Teflon bottles. The sub-samples were digested in 10 mL of Aqua Regia followed by dilution (25 and 50 μL in 50 mL of DI water) and oxidation with BrCl (USEPA, 2002). These samples were analyzed using USEPA Method 1631 and a Tekran 2600 Total Mercury Analyzer (USEPA, 2002).

2.5. Statistical procedures

For each soil TGM sampling period, we calculated daily means of the 10 minute soil temperature, soil moisture, and soil Eh measurements. All plots (N = 3) for each area were combined to calculate a single mean for each depth on each sampling day. This eliminated effects caused by diel fluctuations of variables or sampling time differences. A student's t-test was used to determine if differences existed between

Table 1
A comparison of the soil gas TGM concentrations measured at PRAAMS with other studies.

Soil gas TGM (ng m^{-3})	Maximum (ng m^{-3})	Minimum (ng m^{-3})	Depth	Ecosystem	Study
At PRAAMS:					
4.1 ± 2.0	8.4	1.5	Oe–A interface	Deciduous forest	This study
1.6 ± 1.0	4.6	0.3	A–E interface	Deciduous forest	This study
1.6 ± 0.9	4.3	0.6	5 cm into the E soil horizon	Deciduous forest	This study
1.3 ± 0.7	3.4	0.6	10 cm into the E soil horizon	Deciduous forest	This study
1.5 ± 1.5	5.9	0.5	Oe–A interface	Grass	This study
1.2 ± 1.0	4.2	0.3	A–E interface	Grass	This study
1.3 ± 0.9	3.6	0.5	5 cm into the E soil horizon	Grass	This study
1.6 ± 1.1	4.2	0.4	10 cm into the E soil horizon	Grass	This study
Other studies:					
1 to 2	NR	NR	2 cm	Mixed deciduous and evergreen forest	Sigler and Lee (2006)
3.5 to 6	NR	NR	5 cm	Mixed deciduous and evergreen forest	Sigler and Lee (2006)
0.25 to 2.5	NR	NR	20 cm	Mixed deciduous and evergreen forest	Sigler and Lee (2006)
0.75 to 2	NR	NR	50 cm	Mixed deciduous and evergreen forest	Sigler and Lee (2006)
275 to 310	NR	NR	20 cm	In ECOCELL, Hg enriched soil, before replanting	Johnson et al. (2003)
330 to 360	NR	NR	40 cm	In ECOCELL, Hg enriched soil, before replanting	Johnson et al. (2003)
125 to 175	600	100	20 cm	In ECOCELL, Hg enriched soil, after replanting	Johnson et al. (2003)
175	600	100	40 cm	In ECOCELL, Hg enriched soil, after replanting	Johnson et al. (2003)
137 ± 37	BDL	200	NR	Hg enriched floodplain soils	Wallschläger et al. (2002)
NR	4800	1200	50–70 cm	In Pb–Zn vein type deposits	Kromer et al. (1981)

the early and late samplings within a day. Due to the relatively small sample size, separate one-way ANOVAs were used to determine if differences in soil TGM concentrations existed among depths (all data), plots (all data), and seasons (daily means). All differences in means were significant at the $\alpha = 0.05$ level. Also, all means are reported with $\pm$ one standard deviation from the mean.

3. Results and discussion

3.1. Soil TGM at all depths

Mean soil TGM concentrations for all depths were significantly ($df = 184$, $t = -2.27$, $p = 0.003$) higher in the forest (2.3 ± 2.2 ng m^{-3}) than in the grass field (1.5 ± 1.9 ng m^{-3}) (Fig. 1). These concentrations were in the range of other background soils, but lower than concentrations reported for mercury-enriched soils (Table 1). In the forest, mean soil TGM concentrations for all depths in summer (2.5 ± 2.4 ng m^{-3}) and spring (2.5 ± 2.7 ng m^{-3}) were significantly higher than fall (1.7 ± 1.1 ng m^{-3}) and winter (1.3 ± 1.1 ng m^{-3}). In the grass field, summer (1.8 ± 1.5 ng m^{-3}) and spring (1.6 ± 1.1 ng m^{-3}) TGM concentrations were also significantly higher than fall (0.9 ± 2.4 ng m^{-3}) and winter (0.9 ± 0.6 ng m^{-3}). This seasonal variation was consistent with the seasonal variations of TGM concentrations in red maple, white pine, and oak forests in Coventry, Connecticut (Sigler and Lee, 2006). This pattern may be related to temperature variations (discussed below).

Soil temperature in the forest ranged from 0.4 °C on 1/28/2010 to 19.3 °C on 8/12/2009 (Fig. 2). Soil temperature in the grass field ranged from 0.4 °C on 1/29/2010 to 26.1 °C on 8/10/2009 (Fig. 2). These minimum and maximum soil temperatures occurred at the Oe–A soil interface in each area. Mean daily soil temperatures for all soil TGM

sampling periods were not significantly different between the two areas. Mean daily temperatures were also not significantly different between any two depths in the forest or grass field. This lack of temperature difference was likely due to the open forest canopy and/or shading of the soil by the grass at our grass site. Within each area, soil TGM concentrations increased as soil temperature increased (Fig. 3). This relationship was consistent with that found by Sigler and Lee (2006) and could explain the seasonal differences in soil TGM concentrations. The TGM–temperature relationship could indicate that higher temperatures increased the volatilization of GEM from the soil matrix into the soil pore spaces, leading to higher TGM concentrations in the soils. It is also possible that the higher temperatures stimulated the microbial mediated reduction of Hg(II) to GEM (Baldi, 1997; Fritsche et al., 2008; Kritee et al., 2008).

Soil moisture in the forest reached a minimum of 0.7% at the A–E soil interface on 9/16/2009 and a maximum of 51.4% 5 cm into the E horizon on 1/6/2010 (Fig. 4). Soil moisture in the grass field reached 23.9% at the Oe–A soil interface on 9/14/2009 and 51.3% 5 cm at the A–E interface on 6/2/2010 (Fig. 4). Over the entire campaign at all sampling depths, the grass soils were significantly wetter ($43.1 \pm 6.6\%$) than the forest soils ($32.2 \pm 9.9\%$). Soil moisture at all depths was not correlated with soil TGM concentrations in either area. This could indicate that soil TGM concentrations are unrelated to soil moisture. Alternatively, it is possible that soil moisture induced changes in the soil TGM concentrations were very rapid and undetectable using our 1.5 to 3 hour sampling times.

Soil Eh in the forest reached a minimum of 214 mV on 6/30/2010 at the Oe–A interface and a maximum of 789 mV on 7/28/2009 at the A–E interface (Fig. 5). The grass field soil Eh was at a minimum of 303 mV on 6/2/2010 and a maximum of 743 mV on 9/14/2009 at the A–E interface (Fig. 5). With the exception of the forest Oe–A horizon, soil Eh was not significantly different among sites and depths.
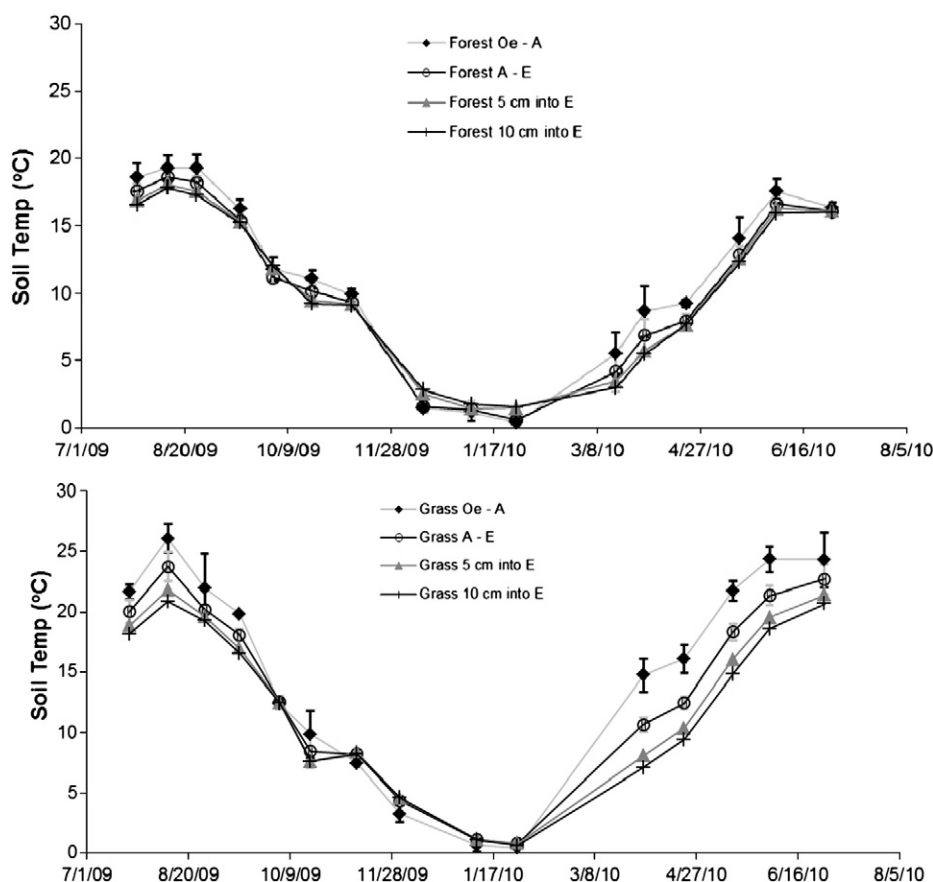

Fig. 2. Mean soil temperature for all depths in the forest (top) and grass field (bottom) during soil gas sampling. Error bars are ± one standard deviation and to simplify the graph error bars are only shown for the Oe–A and A–E soil interface layers (layers with highest standard deviation).
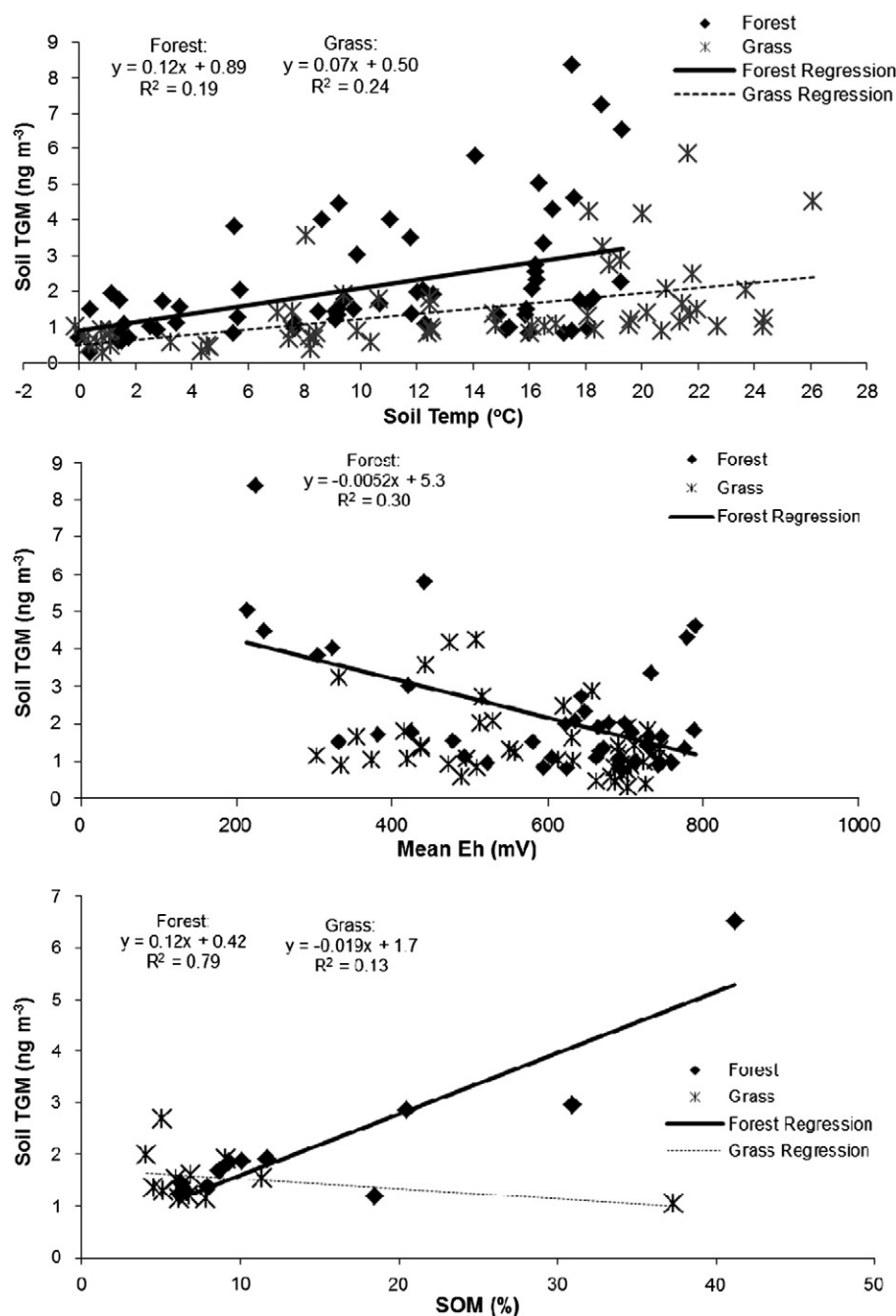
Fig. 3. Soil gas TGM concentration vs. soil temperature (top), Eh (middle), and SOM (bottom). Each data point on the top and middle panels represents a daily mean for each plot in each area. The bottom panel shows the annual mean soil gas TGM at each depth in each plot vs. the soil organic matter content at that depth.

Soil Eh at the forest Oe–A horizon interface (325 ± 90 mV) was significantly lower than the soil Eh in all other soil horizons in both areas (617 ± 128 mV). This increase in soil Eh with depth was similar to that pattern observed in a hardwood forest in Rhinau, France and was linked to nitrate reduction in the shallow soil layers or decomposition of SOM (Brettar et al., 2002). Soil TGM across all depths in the forest increased as soil Eh decreased (Fig. 3). The R^2 for this linear regression was 0.30, but it was statistically significant. Although one of our measurements with a soil TGM concentration of 8.4 ng m^{-3} and a soil Eh of 224 mV appeared to be an outlier, removal of this point still resulted in a statistically significant correlation. However, this relationship was not significant in the grass area (Fig. 3).

The relationship with soil Eh in the forest area was unique. This relationship indicates that soil TGM concentrations in upland forest soils are controlled by the soil redox state, or the balance between

Hg(II) and GEM, rather than the sorption/desorption of GEM. Higher soil TGM concentrations at lower Eh conditions are consistent with the findings of Obrist et al. (2010), who speculated that under anaerobic conditions soil Eh was lowered and more GEM was released from the soil. Our study indicates that the Hg(II)–GEM balance was being influenced by the soil redox potential in our forest soils.

Mean SOM at all depths in both areas except the Oe–A soil horizon interfaces was below 15%. SOM content was $30.9 \pm 10.3\%$ at the Oe–A interface in the forest area. Similar to Sigler and Lee (2006), the soil TGM concentration and SOM at the forest Oe–A interface was the highest of all layers. Mean soil TGM at each depth in the forest increased as SOM increased (Fig. 3). The forest Oe–A horizon had the largest SOM and soil TGM concentration, and resembled an outlier (Fig. 3). When this point was removed, the slope decreased from 0.12 to 0.06 and the R^2 decreased from 0.79 to 0.60. The forest Oe–
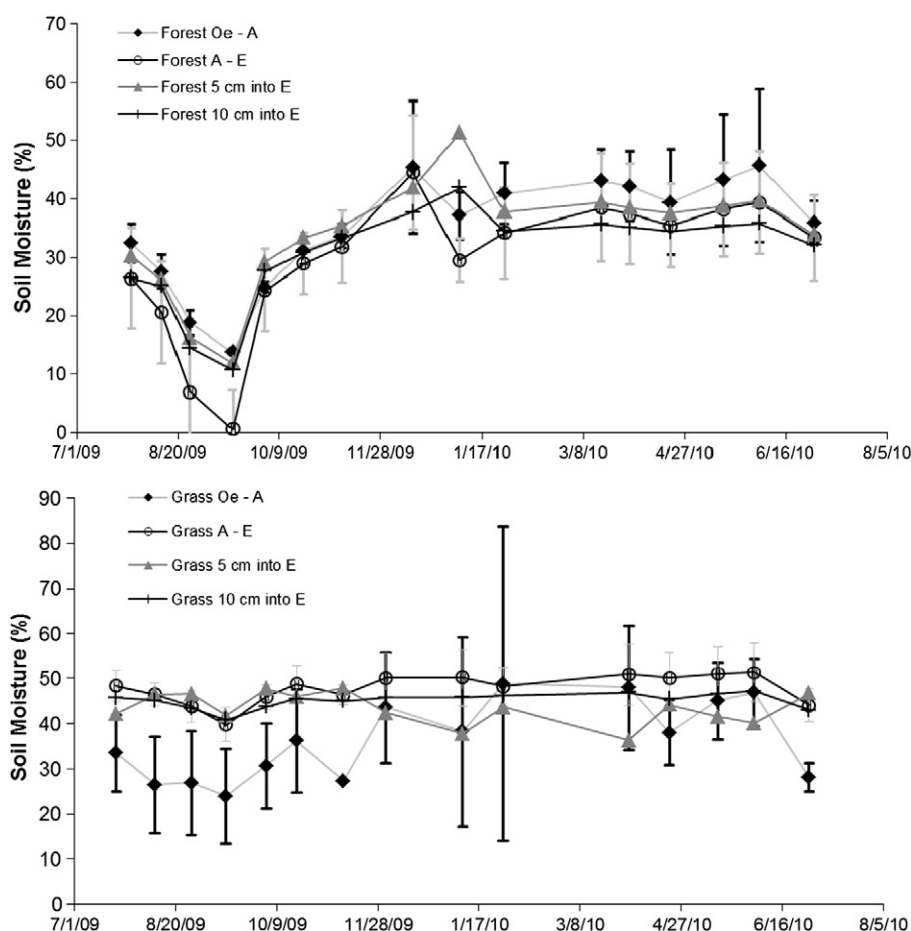
Fig. 4. Mean soil moisture percent for all depths in the forest (top) and grass field (bottom) during soil air sampling. Error bars are ± one standard deviation and to simplify the graph error bars are only shown for the Oe–A and A–E soil interface layers (layers with highest standard deviation).

A interface, with particularly high SOM and soil TGM concentrations, heavily influenced this overall relationship, but even when these points were removed, a statistically significant correlation was still observed. The forest Oe–A interface also had the highest soil bound total mercury concentration (Fig. 6). This was consistent with the findings of others, who suggested that soils with high SOM had higher soil bound mercury concentrations (e.g. Andersson, 1979; Grigal, 2003; Meili, 1991; Obrist et al., 2009).

Mean SOM content at the Oe–A interface in the grass field was 19.3 ± 15.7%. However, the grass field did not have the same positive relationship between soil TGM concentrations and SOM content (Fig. 3). Also, removing the one data point with the highest SOM for the grass field decreased the R^2 reinforcing the lack of relationship between soil TGM concentration and SOM in the grass field. This lack of relationship may indicate that graminoid litter is less effective at controlling the GEM–Hg(II) balance in soils.

3.2. Soil TGM at the forest Oe–A interface

Soil TGM concentrations at the forest Oe–A interface were significantly higher and more variable than the other soil depths in both areas (Fig. 1). Soil temperature and soil moisture were not significantly different between this interface and the other soil layers. Soil Eh was one parameter that distinguished the forest Oe–A interface from all other depths in either area. Throughout our annual sampling period, soil Eh at the forest Oe–A interface remained at or below 400 mV (Fig. 5). Our data suggests that at a soil Eh below 400 mV, soil TGM concentrations increased. This Eh potential is in agreement with Eh–pH diagrams that show that below 400 mV soil bound Hg(II) is reduced to GEM, which can then volatilize into the soil gas

(Andersson, 1979). This transition was also evident in the grass area. When soil Eh dropped below 400 mV on 6/2/2010, the soil TGM concentration at 10 cm into the E horizon rose to 3.2 ng m^{-3}, the highest at that depth for the entire measurement period (Figs. 1 and 4). This would indicate that a threshold Eh of 400 mV for production of TGM exists in the upland soils at PRAAMS.

SOM was also likely playing an important role in soil TGM differences (Gu et al., 2011). The higher SOM content in the forest can be explained by the litterfall inputs from the overstory deciduous trees. Total mercury associated with litterfall was approximately 15 ± 2.1 µg m^{-2} y^{-1}, twice the wet deposition input of mercury (NADP, 2010; Risch et al., 2012). However, throughfall was not measured and can also contribute to higher mercury concentrations in forest soils. These inputs were likely the main reason that the forest Oe–A soil horizon interface had the highest SOM and highest soil matrix bound mercury (Figs. 3 and 5). However, we could not rule out that the wetter conditions in the grass area were leaching both SOM and mercury from the soils, causing the grass area to have lower SOM and bound total mercury. The lower soil matrix bound total mercury concentration at the other soil depths means that there was less Hg(II) available to be reduced to GEM. Based on our observations and those of others (e.g. Gustin et al., 2004; Sigler and Lee, 2006), we suggest that the upper soil horizons in forests with high litterfall inputs and low soil Eh are important sites for the formation of TGM.

4. Conclusions

Seasonal variations in soil TGM in both grass and forest were influenced by soil temperature. Higher temperatures in summer and spring were associated with higher TGM concentrations, while winter and fall showed the lowest TGM concentrations. Soil temperature was
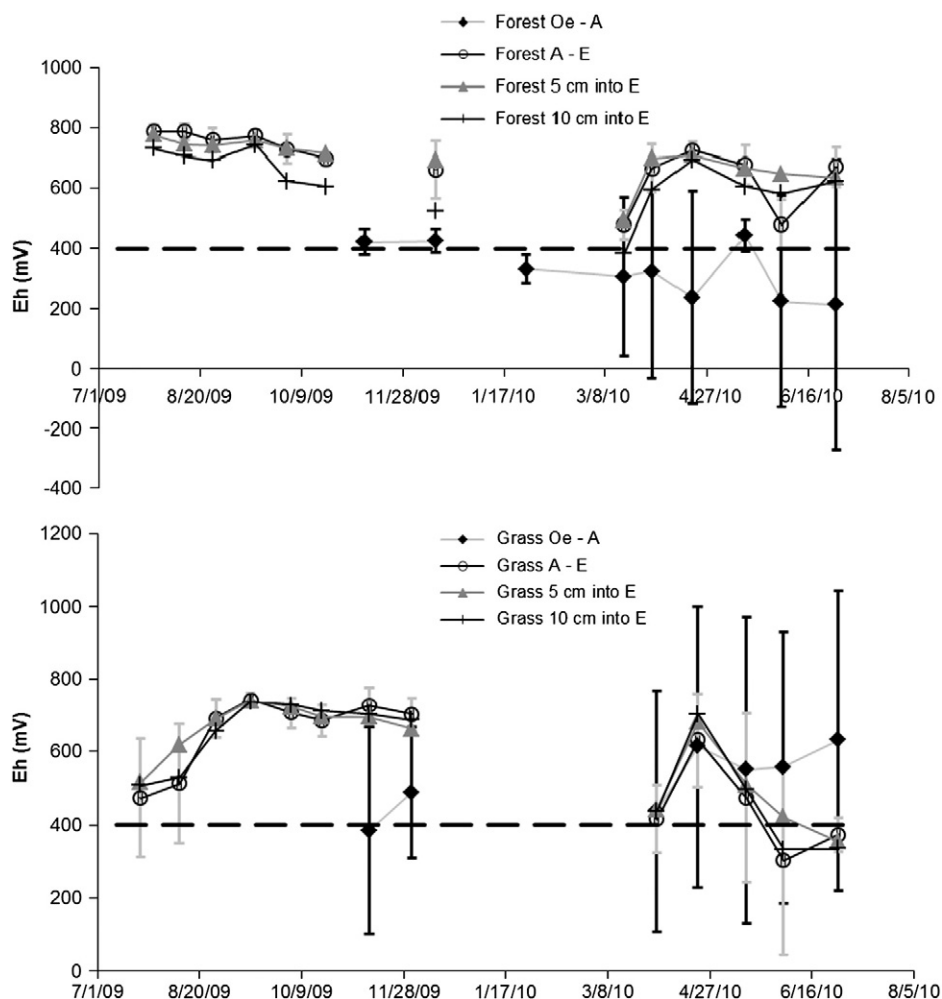
Fig. 5. Mean soil Eh at all depths in the forest (top) and grass (bottom) areas during the times of soil gas TGM sampling at PRAAMS. The dotted line on both panels indicates 400 mV. Error bars are ±one standard deviation and to simplify the graph error bars are only shown for the Oe–A and A–E soil interface layers (layers with highest standard deviation).

consistently correlated with TGM concentrations in the forest and grass areas, but only explained up to 24% of the TGM variability. The Oe–A soil horizon interface showed very different TGM dynamics compared to deeper soils. This layer consistently showed soil Eh potentials below 400 mV, higher SOM content (30.9%), and elevated TGM concentrations. The TGM concentrations at this interface were often 2 to 8 times higher than other layers. These elevated TGM concentrations suggest that TGM was produced at or near this interface when the soil Eh dropped below 400 mV due to the conversion of Hg(II) to GEM. Our results suggest that soil Eh and SOM were significant factors in the retention and formation of TGM within

background forest soils. Future studies of gaseous mercury dynamics in background forest soils may benefit from closely monitoring soil Eh and SOM in the organic soil horizon.

Acknowledgments

Fig. 6. Mean soil bound THg concentration at each depth in each area where soil TGM concentrations were measured. Error bars represent one standard deviation from the mean.

References

Akerblom S, Meili M, Bringmark L, Johansson K, Kleja DB, Bergkvist B. Partitioning of Hg between solid and dissolved organic matter in the humus layer of boreal forests. Water Air Soil Pollut 2008;189:239–52.
Andersson A. Mercury in soils. In: Nriagu JO, editor. The biogeochemistry of mercury in the environment. Amsterdam: Elsevier/North Holland Biomedical Press; 1979. p. 79–122.
Bahlmann E, Ebinghaus R. Process studies on mercury fluxes over different soils with a Laboratory Flux Measurement System (LFMS). J Phys IV 2003;107:99-102.
Baldi F. Microbial transformation of mercury species and their importance in the biogeochemical cycle of mercury. Met Ions Biol Syst 1997;34:213–57.
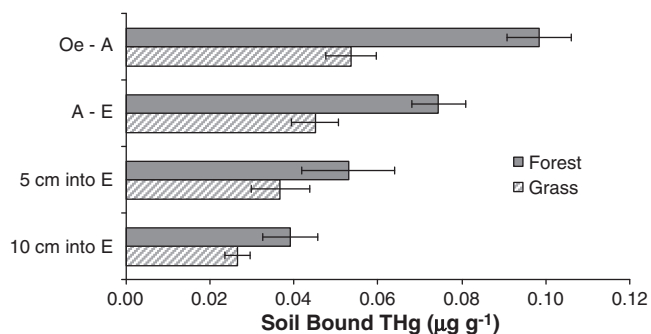
Brettar I, Sanchez-Perez JM, Tremolieres M. Nitrate elimination by denitrification in hardwood forest soils of the Upper Rhine floodplain — correlation with redox potential and organic matter. Hydrobiologia 2002;469:11–21.

Carpi A, Lindberg SE. Application of a Teflon (TM) dynamic flux chamber for quantifying soil mercury flux: tests and results over background soil. Atmos Environ 1998;32:873–82.

Choi HD, Holsen TM. Gaseous mercury emissions from unsterilized and sterilized soils: the effect of temperature and UV radiation. Environ Pollut 2009a;157:1673–8.

Choi HD, Holsen TM. Gaseous mercury fluxes from the forest floor of the Adirondacks. Environ Pollut 2009b;157:592–600.

Demers JD, Driscoll CT, Fahey TJ, Yavitt JB. Mercury cycling in litter and soil in different forest types in the Adirondack region, New York, USA. Ecol Appl 2007;17:1341–51.

Edwards GC, Rasmussen PE, Schroeder WH, Kemp RJ, Dias GM, Fitzgerald-Hubble CR, et al. Sources of variability in mercury flux measurements. J Geophys Res Atm 2001;106:5421–35.

Ericksen JA, Gustin MS, Xin M, Weisberg PJ, Fernandez GCJ. Air–soil exchange of mercury from background soils in the United States. Sci Total Environ 2006;366:851–63.

Fang C, Moncrieff JB. Simple and fast technique to measure CO₂ profiles in soil. Soil Biol Biochem 1998;30:2107–12.

Fritsche J, Obrist D, Alewell C. Evidence of microbial control of Hg⁰ emissions from uncontaminated terrestrial soils. J Plant Nutr Soil Sci Zeitschrift Fur Pflanzenernahrung Und Bodenkunde 2008;171:200–9.

Gabriel MC, Williamson DG. Principal biogeochemical factors affecting the speciation and transport of mercury through the terrestrial environment. Environ Geochem Health 2004;26:421–34.

Gillis AA, Miller DR. Some local environmental effects on mercury emission and absorption at a soil surface. Sci Total Environ 2000;260:191–200.

Grigal DF. Mercury sequestration in forests and peatlands: a review. J Environ Qual 2003;32:393–405.

Gu BH, Bian YR, Miller CL, Dong WM, Jiang X, Liang LY. Mercury reduction and complexation by natural organic matter in anoxic environments. Proc Natl Acad Sci U S A 2011;108:1479–83.

Gustin MS, Stamenkovic J. Effect of watering and soil moisture on mercury emissions from soils. Biogeochemistry 2005;76:215–32.

Gustin MS, Taylor GE, Maxey RA. Effect of temperature and air movement on the flux of elemental mercury from substrate to the atmosphere. J Geophys Res Atm 1997;102:3891–8.

Gustin MS, Ericksen JA, Schorran DE, Johnson DW, Lindberg SE, Coleman JS. Application of controlled mesocosms for understanding mercury air–soil–plant exchange. Environ Sci Technol 2004;38:6044–50.

Johansson K, Aastrup M, Andersson A, Bringmark L, Iverfeldt A. Mercury in Swedish forest soils and waters — assessment of critical load. Water Air Soil Pollut 1991;56:267–81.

Johnson DW, Lindberg SE. The biogeochemical cycling of Hg in forests — alternative methods for quantifying total deposition and soil emission. Water Air Soil Pollut 1995;80:1069–77.

Johnson DW, Benesch JA, Gustin MS, Schorran DS, Lindberg SE, Coleman JS. Experimental evidence against diffusion control of Hg evasion from soils. Sci Total Environ 2003;304:175–84.

Kritee K, Blum JD, Barkay T. Mercury stable isotope fractionation during reduction of Hg(II) by different microbial pathways. Environ Sci Technol 2008;42:9171–7.

Kromer E, Friedrich G, Wallner P. Mercury and mercury — compounds in the surface, air, soil gas, soils, and rocks. J Geochemical Exploration 1981;15:51–62.

Lin CJ, Gustin MS, Singhasuk P, Eckley C, Miller M. Empirical models for estimating mercury flux from soils. Environ Sci Technol 2010;44:8522–8.

Lindberg SE, Zhang H, Gustin M, Vette A, Marsik F, Owens J, et al. Increases in mercury emissions from desert soils in response to rainfall and irrigation. J Geophys Res Atm 1999;104:21879–88.

Meili M. The coupling of mercury and organic-matter in the biogeochemical cycle — towards a mechanistic model for the boreal forest zone. Water Air Soil Pollut 1991;56:333–47.

Moore CW, Castro MS, Brooks SB. A simple and accurate method to measure total gaseous mercury concentrations in unsaturated soils. Water Air Soil Pollut 2011;218:3–9.

NADP. National Atmospheric Deposition Program 2009 annual summary. NADP Data Report 2009–01. Illinois State Water Survey, University of Illinois at Urbana-Champaign, Champaign, IL; 2010.

Nelson DW, Sommers LE. Loss-on-ignition method. In: Sparks DL, editor. Methods of soil analysis part 3. Chemical methods. SSSA Book Series 5. WI: SSSA Madison; 1996. p. 1004–5.

Obrist D, Gustin MS, Arnone JA, Johnson DW, Schorran DE, Verburg PSJ. Measurements of gaseous elemental mercury fluxes over intact tallgrass prairie monoliths during one full year. Atmos Environ 2005;39:957–65.

Obrist D, Johnson DW, Lindberg SE. Mercury concentrations and pools in four Sierra Nevada forest sites, and relationships to organic carbon and nitrogen. Biogeosciences 2009;6:765–77.

Obrist D, Fain X, Berger C. Gaseous elemental mercury emissions and CO₂ respiration rates in terrestrial soils under controlled aerobic and anaerobic laboratory conditions. Sci Total Environ 2010;408:1691–700.

Obrist D, Johnson DW, Lindberg SE, Luo Y, Hararuk O, Bracho R, et al. Mercury distribution across 14 U.S. forests. Part I: spatial patterns of concentrations in biomass, litter, and soils. Environ Sci Technol 2011.

Ponnamperum FN. The chemistry of submerged soils. Academic Press, Inc.; 1972

Rabenhorst AC, Hively WD, James BR. Measurements of soil redox potential. Soil Sci Soc Am J 2009;73:668–74.

Risch MR, DeWild JF, Krabbenhoft DP, Kolka RK, Zhang L. Litterfall mercury dry deposition in the eastern USA. Environ Pollut 2012;161:284–90.

Schluter K. Review: evaporation of mercury from soils. An integration and synthesis of current knowledge. Environ Geol 2000;39:249–71.

Scholtz MT, Van Heyst BJ, Schroeder W. Modelling of mercury emissions from background soils. Sci Total Environ 2003;304:185–207.

Schuster E. The behavior of mercury in the soil with special emphasis on complexation and adsorption processes — a review of the literature. Water Air Soil Pollut 1991;56:667–80.

Sigler JM, Lee X. Gaseous mercury in background forest soil in the northeastern United States. J Geophys Res Biogeosciences 2006:111.

Skyllberg U, Bloom PR, Qian J, Lin CM, Bleam WF. Complexation of mercury(II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups. Environ Sci Technol 2006;40:4174–80.

Song XX, Van Heyst B. Volatilization of mercury from soils in response to simulated precipitation. Atmos Environ 2005;39:7494–505.

Tsiros IX. Modeling assessment of air emission flux of mercury from soils in terrestrial landscape components: model tests and sensitivities. J Air Waste Manage Assoc 2002;52:339–48.

USDA. Web soil survey. http://websoilsurvey.nrcs.usda.gov/app/WebSoilSurvey.aspx, 2009.

USDA-NRCS. NRCS soil quality; 2011.

USEPA. Method 1631, revision E: mercury in water by oxidation, purge, and trap, and cold vapor atomic fluorescence spectrometry; 2002.

van Bochove E, Beauchemin S, Theriault G. Continuous multiple measurement of soil redox potential using platinum microelectrodes. Soil Sci Soc Am J 2002;66:1813–20.

Wafer CC, Richards JB, Osmond DL. Construction of platinum-tipped redox probes for determining soil redox potential. J Environ Qual 2004;33:2375–9.

Wallschläger D, Kock HH, Schroeder WH, Lindberg SE, Ebinghaus R, Wilken R-D. Estimating gaseous mercury emissions from contaminated floodplain soils to the atmosphere with simple field measurement techniques. Water Air Soil Pollut 2002;135:39–54.

Yin YJ, Allen HE, Huang CP, Sparks DL, Sanders PF. Kinetics of mercury(II) adsorption and desorption on soil. Environ Sci Technol 1997;31:496–503.

Zarate-Valdez JL, Zasoski RJ, Lauchli A. Short-term effects of moisture content on soil solution pH and soil Eh. Soil Sci 2006;171:423–31.

Zhang H, Lindberg SE. Processes influencing the emission of mercury from soils: a conceptual model. J Geophys Res Atm 1999;104:21889–96.